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PROCEEDINGS
OF THE
AMERICAN ACADEMY
OF
ARTS AND SCIENCES.

VOL. XVII.

PAPERS READ BEFORE THE ACADEMY.

I.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

BY JOSIAH PARSONS COOKE, *Director*.

Presented May 11, 1881.

INTRODUCTION.

In a paper presented to the Academy, and published in its proceedings, Vol. XIII., page 1, we gave the results of our investigation of the haloid compounds of antimony up to that time, including a revision of the atomic weight of this element. We did not directly answer the criticism which this paper called forth, except so far as to present to the Academy, March 10, 1880, and to publish in these Proceedings, Vol. XV., page 251, a preliminary notice of experiments then in progress which furnished the best possible answer to the unfounded assumptions of the critic. We also gave brief notices of our work from time to time in the American Journal of Science. But now that the work is ended for the present (or at least must be suspended for a considerable period), we propose to bring the results together in the present paper.

I. THE OXIDATION OF HYDROCHLORIC ACID SOLUTIONS OF
ANTIMONY IN THE ATMOSPHERE.

In our first paper (*loc. cit.*, page 21) we made the following incidental observation, in explanation of certain precautions which we

found to be necessary in order to secure the precipitation of pure antimonious sulphide :—

“The precautions here described may seem unnecessary to those who are not familiar with the fact that a solution of antimony in hydrochloric acid oxidizes with very great rapidity in the air,—fully as rapidly as the solution of a ferrous salt. A solution reduced as we have described, which has at first no action on the iodized starch paste, will strike the blue color after it has been exposed to the air for only a few minutes. This property of an acid solution of antimonious chloride is mentioned by Dexter, in the paper already referred to, but we were wholly surprised by the energy of the action. By means of it, antimony can be dissolved in hydrochloric acid without the aid of nitric acid, or of any other oxidizing agent save the air, if only a certain amount of antimonious chloride has once been formed. When, after exposure to the air, the solution is boiled over pulverized antimony, the solution is reduced, and a further portion of the metal enters into solution. After a second exposure, the same process can be repeated, and so on indefinitely. The process is very slow and tedious, but, in one experiment, we succeeded in bringing into solution in this way several grammes of antimony.”

On the sole basis of this language we have been represented as asserting that such antimony solutions oxidize in the air as rapidly as a solution of *ferrous chloride*, and experiments on comparatively dilute solutions of antimonious oxide in hydrochloric acid have been adduced as proofs that our observation was incorrect.

As is evident from the context, the statement just quoted, although the result of a very extended experience, was not based on quantitative measurements. What we noticed was that the solutions *were very quickly acted on* by the oxygen of the atmosphere, and we freely admit that the expression here italicized is a more accurate description of our observation than the words originally used as quoted above. But our meaning was not left in doubt, for we expressly say, immediately after, that the process is very slow and tedious. In regard to the phenomenon in question, the effects are so obvious, when once attention is called to them, that it is entirely unnecessary to confirm our previous observations except so far as to add the following quantitative determinations, which will serve to give an accurate idea of the extent of the action under the only conditions we have investigated, or in regard to which we have written.

In order to determine the amount of oxidation caused by the action of the atmosphere on a solution of antimony in hydrochloric acid, we

reduced the oxidized solution by boiling the liquid over antimony bullets, and determined the loss in their weight. This method is fully described in our original paper, and is based not only on the reducing power of the metal, but also on the fact repeatedly observed, that, after the reduction was complete, the smallest excess of the finely pulverized metal would not dissolve, even after prolonged boiling, and in the presence of a large excess of acid, if only the solution was protected from oxidation.

We began our experiments by dissolving 1.0036 grammes of pure antimony (a portion of the same used in our experiments on the synthesis of antimonious sulphide) in about 30 cubic centimetres of pure hydrochloric acid (sp. gr. = 1.175) adding 3 cubic centimetres of very dilute nitric acid (containing only about 5.4 per cent of HNO_3). After the solution was completed we added bullets made of pure antimony (the same that had been used in our previous experiments), and boiled the solution in an atmosphere of carbonic dioxide, using the same apparatus which we described in our previous paper (*loc. cit.*). After the reduction was ended, the solution was transferred to a flat-bottomed flask through a platinum tunnel, on which the bullets were retained; and, after washing into the flask the last traces of the solution, with as small an amount of hydrochloric acid as possible, the tunnel was removed, the bullets washed with water, and again weighed as at first on the platinum tunnel. In reducing the original solution, 0.4100 of a gramme of antimony were dissolved from the bullets. The solution now containing 1.4136 grammes of antimony was next exposed to the air for different successive periods of time in a room having a varying temperature of from 15° to 30° , sometimes in the shade, and at other times on a window seat, where the sun's direct rays fell on the flask during several hours of each clear day.

We give in the following table the weight of antimony dissolved from the bullets after each successive exposure to the air, the amounts in each case being determined with all the precautions described above, and still more at length in our former paper:—

Weight of Sb originally dissolved		1.4136
1.	Dissolved from balls after 3 days' exposure,	0.0150
2.	“ after 5 days	0.0295
3.	“ “ 10 “ May 17 to May 27 .	0.0600
4.	“ “ 23 “ May 27 to June 19 .	0.1340
5.	“ “ 37 “ June 19 to July 26 .	0.2960
6.	“ “ 120 “ July 26 to Dec. 24 .	0.4481 0.9826

During these experiments the volume of the solution was gradually increased by the hydrochloric acid used in washing as above described, so that at last the volume amounted to 100 cubic centimetres.

It will be noticed that the amount of oxidation increased with the time of exposure, and that, so long as the amount was small, it was as nearly proportional to the time as could be expected under the varying conditions. The increased activity shown by determination No. 5 appeared to be due to the intensely warm weather and bright sunshine during the period, and the last determination would seem to indicate that, after the oxidation reached a certain limit, the process went on more slowly, as we should naturally expect; but, with the greatly varying conditions during this long period, no certain conclusion can be drawn in regard to the effect of any single cause.

The action we are discussing is entirely in harmony with the chemical relations of antimony. The most striking characteristic of this elementary substance is its tendency to form compounds of the radical antimonyl, SbO . The oxichlorides, the oxibromides, and the oxiodides, whose relations we have discussed so fully in our previous papers, are examples in point, and we have been continually surprised by the appearance of such compounds in reactions in the most unexpected ways. In this respect antimony closely resembles vanadium, and with this element antimony is more closely allied than with its familiar associate, arsenic. What the precise reaction is in the present case we are not prepared to state. That it is not the simple conversion of a terchloride into a pentachloride we are convinced; but, in order to elucidate the subject, further investigations are necessary.

In this connection we may appropriately add that while the above determinations were in progress we repeated the experiment described on page 19 of our previous paper (*loc. cit.*). We treated in an open flask 5 grammes of finely powdered pure metallic antimony with 50 cubic centimetres of strong and pure hydrochloric acid, to which we added only one cubic centimetre of the very dilute nitric acid (5.4 per cent) described above. The flask was placed in a warm, protected place (30°C.), and shaken from time to time. Soon the acid became colored reddish-yellow, and the chemical action began. When it had apparently ceased, the contents of the flask were shaken together, and the solution became at once as colorless as water; but, on standing in the air, the color rapidly returned, spreading from the surface of the liquid downward. These phenomena were repeated again and again during four or five months, until the whole of the metal dissolved. According to the reaction usually assumed to take place under these

circumstances, 5 grammes of metal would have required 50 cubic centimetres of acid, so that the effect was obtained with only one-fiftieth of the amount required by this theory.*

II. ARGENTO-ANTIMONIOUS TARTRATE (SILVER EMETIC).

On one occasion when analyzing antimonious chloride we noticed the formation of "silver emetic," and the observation led us to fear that this compound might be occluded by the argentic chloride or bromide, precipitated from a solution containing tartaric acid and antimony. This suspicion, thus excited, led us to make an investigation of the substance in question with the following results:—

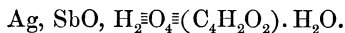
As stated by us in our former paper, this compound was originally obtained by Wallquist by precipitating nitrate of silver with tartar-emetic, and was analyzed both by him and by Dumas and Piria. These chemists obtained respectively 27.31 and 28.05 per cent of oxide of silver. They appear, however, to have prepared the substance only in an amorphous form. As stated in the paper just cited, we first noticed the formation of crystals of the compound in a concentrated solution of antimonious chloride and tartaric acid, to which had been added an excess of argentic nitrate, and from the circumstances of their formation we were led to form a somewhat erroneous inference in regard to their relation to water. We find that the substance is far more soluble in this solvent than at first appeared. We have found from further investigation that one part of silver emetic dissolves completely in one hundred parts of boiling, and in somewhat less than five hundred parts of water at 15° C. In one determination made by evaporating, a saturated solution, which had stood a long time at a temperature of 15°, we found that one thousand parts of water had dissolved 2.76 parts and in another 2.68 parts of the salt. There

* Although in our synthesis of antimonious sulphide it was our constant study from the first to prevent the oxidation of the product, and although we most carefully guarded every phase of the process, yet the theory was advanced that the apparent weight of the product was *increased* by a partial oxidation of the antimonious sulphide at the temperature at which the red was converted to the gray modification. In answer to this wholly gratuitous assumption, it is only necessary to say: 1. That the oxidation of the dried precipitate at this stage of the process is a well-marked phenomenon, with every phase of which we are acquainted. 2. That the oxidation is always attended with a *loss* of weight. 3. That the products of our determinations were always examined, and have been in two cases preserved, and that these do not show the least signs of oxidation.

is obviously therefore no danger of the formation of this product in the precipitation of chlorine, bromine, or iodine from solutions of the antimony compounds of these elements in tartaric acid, unless the excess of silver nitrate is very large and the solutions very concentrated; and although we have most carefully looked for it in the precipitate we have never discovered it, except under the peculiar conditions described in our former paper, and our fear that it might be occluded by these precipitates was wholly unfounded.

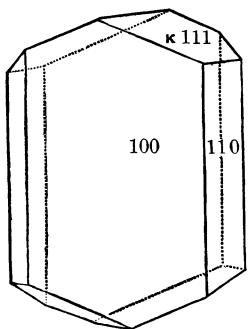
It is evident from the above experiments that the solubility of silver emetic in water like that of cream of tartar and other salts of tartaric acid is very greatly increased by heat, and we were easily able to obtain good crystals of the compound in large quantities by dissolving the precipitate, obtained as Wallquist describes, in boiling water, and allowing the solution to cool. The crystals are colorless and have a very brilliant, almost an adamantine, lustre.

From the reaction by which silver emetic is formed we should infer that the composition of the salt would be expressed by the symbol



This compound would theoretically contain 26.34 per cent of silver and, as a mean of three analyses, we obtained for the amount of silver in the crystals 26.30 per cent, as previously stated.

The crystals of silver emetic rapidly blacken in the light, and are very easily decomposed by heat. This decomposition takes place at about 200° C. with a slight explosion. A very fine carbon dust is blown out of the crucible, and a residue is left behind, which under the microscope is seen to consist of spangles of metallic silver mixed with an amorphous powder. Almost the whole of the powder dissolved easily in a solution of tartaric acid, and it evidently consisted of Sb_2O_3 . In one experiment we weighed the silver emetic and the product, and found that 0.8460 gramme of the salt left 0.5304 gramme of residue. If the residue consisted solely of silver and Sb_2O_3 ,



theory would require 0.5200 gramme, and it can be seen from this how perfect the decomposition was. It is obvious, therefore, that were this compound occluded as we at first feared, it would have made itself evident on drying the precipitates.

Mr. W. H. Melville, assistant in this laboratory, has made the fol-

lowing crystallographic measurements of the crystals whose formation and reactions we have described.

Angles between normals.

$$\begin{aligned}(111) \wedge (100) & 70^\circ \quad 19\frac{1}{3}' \\ (111) \wedge (111) & 70^\circ \quad 17' \\ a : b : c & = 1 : 1.386 : 0.571\end{aligned}$$

	I.	Measured.
100 \wedge 110	54° 12'	54° 19'
111 \wedge 110	54° 51'	54° 54'

The pinacoid planes were irregular and the angles can only be regarded as approximate.

System Trimetric with hemihedral habit.

Observed planes $+ \kappa \{111\} \{100\} \{110\} \{011\} ?$

In the following table the crystallographic ratios are compared with those of the acid tartrates of rubidium, caesium and potassium, formerly measured by us, and which have the same general form and hemihedral habit.

	Vertical.	Macro.	Brachy.
Acid tartrate of caesium . . .	0.661	1	0.694
“ “ rubidium . . .	0.695	1	0.726
“ “ potassium . . .	0.737	1	0.711
Silver emetic	0.412	1	0.721

III. ON THE SOLUBILITY OF ARGENTIC CHLORIDE IN WATER.

In our analyses of antimonious chloride we constantly noticed, while washing the precipitated chloride of silver with warm water, that although the water first decanted from the precipitate was perfectly clear it became turbid when mixed with the successive washings; and on investigating the cause of this unexpected result we found that it was due to the chloride silver dissolved by the pure wash water and reprecipitated by the excess of nitrate of silver in the filtrate. As the solvent action of the water used for washing the precipitate evidently produced a marked effect on our chlorine determination, we determined at once to investigate the extent of the influence.

This subject has already been studied by Stas, whose observations are summed up by Dr. John Percy* in his recent volume on the Metallurgy of Silver in the following words:—

* Metallurgy of Silver and Gold, Part I. p. 60.

"The solubility of the chloride is greatest when in the flaky state, as precipitated in the cold from a sufficiently dilute solution of silver; the solubility diminishes as the flakes shrink when left to themselves, or as they are rendered pulverulent by long agitation with water. Flaky or pulverulent chloride of silver, dissolved in water, pure or acidified by nitric acid, is precipitated by the addition of a salt of silver, or of hydrochloric acid, or of an alkaline chloride. . . . The solution of the chloride is wholly effected by pure or acidified water, as the case may be, and is not caused by the soluble salt formed simultaneously with the chloride of silver. The presence of nitric acid in the water does not affect the solubility of flaky chloride of silver; but it increases the solubility of the pulverulent chloride in proportion to the quantity of acid present. The precipitation of the dissolved chloride is the exclusive result of its insolubility in the solution formed by adding an excess either of the silver salt or of the alkaline chloride."

So also in Liebig and Kopp, *Jahresbericht*, 1871, 339: "According to Stas, the granular scaly and crystalline chloride is wholly insoluble in cold water: in boiling water the solubility is comparatively great, but decreases rapidly with the temperature."

In our own investigation of this subject we have at once confirmed and extended these observations of Stas, and our results may be of interest as showing that in the very familiar method of determining chlorine by precipitation with nitrate of silver, which is generally supposed to be extremely accurate, a sensible error may arise from the solubility of the chloride of silver in the hot distilled water used in washing the precipitate. It would be well for every analyst to make the following very striking experiment, which will enable him to appreciate the extent of the action in question.

Take from five to ten cubic centimetres of pure hydrochloric acid, and precipitate the chlorine in the usual way with nitrate of silver, avoiding a large excess. After pouring off the supernatant liquid and washing the precipitate once or twice with cold distilled water, pour upon the white flaky chloride of silver a comparatively large volume of boiling water. As soon as the precipitate settles, pour off the clear hot water, dividing the solution between two precipitating jars. To one of these add a few drops of a solution of nitrate of silver, and to the other a few drops of hydrochloric acid. In both cases a precipitate of chloride of silver will fall, and most chemists, certainly, will be surprised at the effect; for it is not a mere turbidness that results, but a well-defined precipitate, whose amount is easily estimated. Successive portions of boiling water poured upon the precipitate give the

same reaction. In one experiment the reaction was still perceptible in the fourteenth wash-water. But under the action of the boiling water, the precipitate becomes crystalline or granular and the action lessens, until at last the water does not dissolve sufficient chloride of silver to cause even a cloudiness on the addition of nitrate of silver, as just described. Mr. G. M. Hyams, a student in this laboratory, washed two different portions of chloride of silver with boiling water until the action ceased, and then weighed and examined the residue. In the first experiment 1.4561 grammes of chloride of silver were washed with 66 litres of water. The chloride of silver was then collected, and found to weigh 1.2320 grammes. Hence, 0.2241 gramme, corresponding to 15.39 per cent, had passed into solution. In the second experiment 60 litres of water were used, and 16.03 per cent of the chloride of silver originally precipitated were dissolved. These numbers, however, are only approximately accurate; for, as the precipitate becomes granular, it settles with less readiness, and there was necessarily some loss in filtering off so large a volume of liquid.

In the experiments above described the boiling water produced only a very slight decomposition of the chloride of silver. The precipitate, granulated by the washing, readily dissolved in aqua ammonia, leaving less than a milligramme of a black powder, which was proved to be metallic silver.

The solvent power of water on freshly precipitated chloride of silver did not appear to be influenced by the presence of free nitric acid, even in large quantities. We tried the effect both of dropping the nitric acid on the precipitate before pouring on hot water, and also of previously adding nitric acid to the boiling wash-water. We used amounts of nitric acid ($\delta = 1.355$) varying from five to two hundred cubic centimetres to the litre of water, but without finding any marked difference in the result.

The presence of a small amount of nitrate of silver in the water entirely prevented its solvent action, so far as we could discover. In order to determine the limit of the action, we added different quantities of nitrate of silver to the boiling water before pouring it on to the precipitated chloride of silver. With one centigramme of nitrate of silver to the litre of water, there was a marked turbidness on subsequently adding an excess of the same reagent to the filtrate. With two, three, or even four centigrammes to the litre, an opalescence could still be distinguished, although constantly diminishing with the increasing amount of the salt. With five centigrammes, there was no opalescence, and we concluded that one decigramme of nitrate of

silver to the litre of boiling wash-water would certainly prevent all action.

A few drops of hydrochloric acid added to the wash-water greatly diminishes its solvent action on flaky chloride of silver, but does not wholly prevent it, as is evident from the fact shown in the table below, that hydrochloric acid does not precipitate chloride of silver from its solution in water nearly as effectually as nitrate of silver; and, as is well known, hydrochloric acid, if in any considerable excess, exerts a strong solvent action on the precipitated chloride.

As shown by Stas, the precipitation of chloride of silver, from its solution in hot water by the reagents we have named, depends solely on the change which the reagents produce in the solvent. That the action is an example of simple solution is shown by the fact that a considerable portion of the chloride of silver dissolved in boiling water is deposited when the solvent cools. This phenomenon is a striking one, and can easily be observed by pouring into a glass crystallizing pan some of the clear solution obtained in the experiment described above. As the water cools it becomes cloudy, and deposits a granular powder, which adheres to the bottom of the glass. The grains are usually very small; but if the solution cools slowly the crystalline form can readily be distinguished under the high powers of a good microscope, and the little cubes present all the characteristics of the native crystals of chloride of silver. It is evident, therefore, that the granular condition of chloride of silver is a crystalline condition, and this experiment may elucidate the manner in which the native crystals are produced.

We have thus far only spoken of the solubility of chloride of silver in boiling water. As is evident from the crystallization just described, the solubility rapidly diminishes as the temperature falls; but even at the ordinary temperature the solubility is distinctly marked. Luke-warm water poured on and off freshly precipitated chloride of silver, becomes decidedly opalescent on the addition of nitrate of silver, and even if cold water is used the opalescence is perceptible.

In order to obtain an approximate measure of the effects we have described, Mr. Hyams precipitated about fifteen grammes of chloride of silver, and, after thoroughly washing it, boiled the precipitate with a large volume of water in a glass flask. At the end of an hour he decanted through a filter about one litre of the boiling water, and, having divided the filtrate into two portions, he added to one portion nitrate of silver, and to the other, hydrochloric acid. The precipitated chloride of silver was in each case collected and weighed. At the end

of two hours' boiling, two other portions were filtered off and treated in a similar way. These determinations were then repeated with a fresh quantity of chloride of silver, and afterwards taking a third quantity of chloride of silver, the boiling water was simply poured on twice in succession, and the similar portions thus obtained treated as before. The results in every case were nearly the same as shown in the following table. In this table

1 and 2 are results after one hour's boiling of 1st quantity.
 3 and 4 " " " two hours' " " " "
 5 and 6 " " " one hour's " " 2d quantity, etc.
 7 and 8 " " " two hours' " " " "
 9 and 10 after simply pouring on boiling water.
 10 and 12 " " " " " "

No.	Wght of Water.	Wght of AgCl.	Wght of AgCl per litre.	Precipitant.
1	523.6 gram.	0.0011	0.0021	Nitrate of silver.
2	469.5	0.0004	0.0009	Hydrochloric acid.
3	115.0	0.0002	0.0017	Nitrate of silver.
4	402.1	0.0004	0.0010	Hydrochloric acid.
5	225.0	0.0004	0.0018	Nitrate of silver.
6	462.0	0.0004	0.0009	Hydrochloric acid.
7	696.4	0.0014	0.0020	Nitrate of silver.
8	825.4	0.0007	0.0008	Hydrochloric acid.
9	700.4	0.0014	0.0020	Nitrate of silver.
10	747.2	0.0007	0.0009	Hydrochloric acid.
11	520.9	0.0011	0.0021	Nitrate of silver.
12	287.5	0.0003	0.0010	Hydrochloric acid.

If we assume that the amount of chloride of silver precipitated by nitrate of silver under the conditions described above is a correct measure of the solubility of the chloride, it appears from the above determinations that about two milligrammes of chloride of silver are dissolved by each litre of boiling water, and further that only about one half of the amount thus dissolved is precipitated by hydrochloric acid.

In making chlorine determinations, it is a very common practice to wash with very hot water, in order to secure the prompt settling of the chloride of silver, or to wash away any occluded material, and it was the chief object of this investigation to determine the extent to which the solubility of the chloride in distilled water might affect the result. For this purpose we made two series of determinations

of the chlorine in chloride of antimony; in both cases precipitating with nitrate of silver the chlorine from a solution of the chloride of antimony in tartaric acid and water with the usual precautions. But, while in the first series the precipitated chloride of silver was washed with boiling hot distilled water to about the $\frac{1}{100,000}$ according to Bunsen's scheme; in the second series, although hot water was also used in washing, one decigramme of nitrate of silver per litre was added to each successive portion of the wash-water poured upon the precipitate, until the last two portions, which were poured on cold. By this simple device, the advantages of washing with hot water may be secured, while its solvent action is prevented. The results are given in the following table:—

FIRST SERIES.

No.	Weight of SbCl_3 taken.	Weight of AgCl obtained.	Per cent of Cl calculated.
1	2.3856 gram.	4.4784 gram.	46.441
2	3.1300	5.8712	46.407
3	3.4207	6.4243	46.462
4	5.0031	9.3790	46.377
Mean value,			46.422
Max. diff. from mean,			0.047

SECOND SERIES.

No.	Weight of SbCl_3 taken.	Weight of AgCl obtained.	Per cent of Cl calculated.
1	3.4059 gram.	6.4188 gram.	46.624
2	3.6603	6.9014	46.643
3	2.4762	4.6658	46.617
4	2.5567	4.8212	46.651
Mean value,			46.634
Max. diff. from mean,			0.017
Difference between means of two series,			0.212

It is evident from these results that when great accuracy is required, the solubility of chloride of silver may become a very serious source of error in determinations of chlorine, and in our first paper on the atomic weight of antimony, this was the chief cause of the discrepancy between the analyses of chloride of antimony on the one hand, and the bromide, iodide, and sulphide of antimony—analyses of which closely agreed among themselves—on the other hand. It was shown in the paper just referred to that, although the greatest care was taken in purifying the material, the chloride of antimony used actually left

behind on evaporation a sufficient amount of oxichloride to reduce the per cent of chlorine 0.116 (loc. cit. page 64). The mean results which we actually obtained from seventeen analyses of chloride of antimony was 46.620; and when to this we add 0.212 and 0.116, the sum is 46.948, which differs from 46.985 — the theoretical value when $\text{Sb} = 120$, and $\text{Cl} = 35.457$ — by only 0.037, or if we take $\text{Cl} = 35.5$ by 0.072. In this estimate we leave out of the account the known solvent action on chloride of silver of the tartaric acid used to keep the antimony in solution. This must equally affect both of the series of determinations given above, and fully accounts for the small difference that remains to be explained. This whole discussion, however, only serves to confirm the conclusion previously expressed, that chloride of antimony is a most unsuitable material for the basis of an atomic weight determination; and, having explained the anomaly to which we gave prominence in a previous paper, we shall here take leave of the subject. We have also studied the solubility of bromide of silver in water, but this is so small that we found it difficult to measure the amount. In water at the ordinary temperature, or even in tepid water, bromide of silver is practically insoluble. In boiling water it is perceptibly soluble, but not more so than is chloride of silver in water at the ordinary temperature. Hence the determination of bromine does not require the same precautions, and is susceptible of greater accuracy than that of chlorine; and on this account, as well as for other reasons which we have previously discussed, the atomic weight of antimony can be deduced from the analyses of the bromide of antimony with as great accuracy as can at present be reached in such determinations. In the seven determinations of the per cent of bromine in bromide of antimony, whose results are given beyond (p. 18), the maximum difference from the mean value 66.6651 was only 0.0045, and Professor Mallet, in his analyses of bromide of aluminum, has obtained with the same method a similar degree of accuracy.*

In conclusion, we would again express our obligations to Mr. G. M. Hyams, who has assisted us in the work of this investigation.

IV. ADDITIONAL EXPERIMENTS ON THE ATOMIC WEIGHT OF ANTIMONY.

In our previous paper on this subject, we gave our reasons for the opinion, since fully confirmed, that the bromide of antimony is the

* Philosophical Transactions, Part III. 1880, 1022.

most suitable compound of this element, as yet known, for determining its atomic weight; and the results of fifteen analyses of five different preparations of the bromide were published, which gave for the atomic weight in question the mean value 120.00 with an extreme variation between 119.4 and 120.4 for all the fifteen analyses, and between 119.6 and 120.3 for the six determinations in which we placed most confidence. The antimonious bromide used in these determinations was purified first by fractional distillation, and secondly by crystallization from a solution in sulphide of carbon. In the crystallized product thus obtained, the bromine was determined gravimetrically as bromide of silver in the usual way. Although it seemed at the time that the results were as accordant as the analytical process would yield under the unfavorable conditions, which the presence of a large amount of tartaric acid in the solution of the bromide of antimony necessarily involved; yet it was obvious that the agreement was far from that which was desirable in the determination of an atomic weight, and our chief confidence in the accuracy of the mean value — independently of its remarkable agreement with previous results — was based on the fact that the known sources of error tended to balance each other. Hence our conclusions were stated with great caution, and the hope was expressed that, after a more thorough investigation of the subject, we might be able “to return to the problem with such definite knowledge of the relations involved as will enable us to obtain at once more sharp and decisive results than are now possible.”

In our previous paper, we described a simple apparatus which we devised for subliming iodide of antimony; and in a note to the paper we stated that we were applying the same process to the preparation of bromide of antimony, and that it promised excellent results. Our expectations in this respect have been fully realized, and the product leaves nothing to be desired, either as regards the beauty or the constancy of the preparation. The fine acicular crystals are perfectly colorless, and have a most brilliant silky lustre. With ordinary precautions, they can be kept indefinitely without change, and it is easy therefore to determine the weight of the material analyzed to the tenth of a milligramme.

The material used in the following determinations was first prepared as described in our previous paper. It was then repeatedly distilled from a small glass retort rejecting at each distillation the first and the last portion. Lastly, it was twice sublimed in a slow current of absolutely dry carbonic dioxide. As it was only possible to sublime a

few grammes at a time in the apparatus we used, and as the several products were not mixed, each of the portions analyzed was the yield of a separate sublimation, and the agreement of the results is therefore in itself a proof of the constancy of the preparation. In the first set of analyses, the bromine was determined gravimetrically by precipitation with nitrate of silver, as before described. The bromide of antimony was first dissolved in a concentrated solution of tartaric acid, using about five grammes of the crystallized acid to a gramme of the bromide, and the solution was then diluted with from 250 to 500 cubic centimetres of water. To this solution was slowly added, under constant agitation, a solution of nitrate of silver in slight excess of the amount required for complete precipitation. The amount of crystallized nitrate of silver required was always carefully weighed out, allowing one decigramme in excess of theory for every litre of the solution of bromide of antimony made as above described. The nitrate of silver was then dissolved in a considerable volume of water, and the bromide of silver was precipitated from a cold solution, care being taken to prevent the formation of lumps which invariably result if the solutions are warm or concentrated, and which greatly interfere with the washing of the precipitate. The precipitate was washed by decantation five times, pouring on in each case a volume of lukewarm distilled water equal to that of the original solution, and after the precipitate had settled, drawing off the wash-water with the inverse filter (see these Proceedings, Vol. XII. page 124.) Lastly, the precipitate was transferred to a porcelain crucible, and dried at from 120° to 130° .

The bromide of silver weighed was always tested, sometimes by dissolving the material in strong aqua ammonia, and at other times by heating it to the melting point. Had there been the least occlusion of silver emetic, or any other possible product, there would have been an insoluble residue or a loss of weight; and, since the bromide of silver always gave a perfectly clear solution, and the loss of weight on melting never exceeded a few tenths of a milligramme, we were assured that our product was perfectly pure.

Of the five determinations whose results are given below, the first three were made under my direction by Mr. G. De N. Hough; the last two were made with my own hands.

ANALYSES OF ANTIMONIOUS BROMIDE.

Determination of Bromine.

No.	Wt. of SbBr ₃ taken in grammes.	Wt. of AgBr obtained.	Per cent of Br. Br = 80 Ag = 108.	Diff. from mean.	Value of Sb.	Diff. from mean.
1.	4.1767	6.5420	66.652	— 0.016	120.08	+ 0.08
2.	2.0250	3.1734	66.685	+ 0.007	119.90	— 0.10
3.	1.9999	3.1340	66.680	+ 0.012	119.93	— 0.07
4.	3.6985	5.7946	66.669	0.001	119.99	— 0.01
5.	2.8959	4.5361	66.653	0.015	120.08	+ 0.08
Mean value			66.6679		119.996	
Theory Sb. 120 requires			66.667			

The mean value of the percentage of bromine deduced from the fifteen analyses previously made (see these Proceedings, Vol. XII., page 54) was 66.666, which differs only by an inappreciable quantity from the mean of the above results. At the same time the results are much sharper, the maximum difference from the mean value having been reduced to less than one fifth of the previous amount, and to only 0.00025 of the quantity estimated, giving us with certainty the atomic weight of antimony within one one-thousandth of its value. It must be remembered, moreover, that, although these last results were obtained with the same compound as before, the material was prepared in a wholly different way. The material first used was purified by repeated crystallization from sulphide of carbon,— that last used by repeated fractional distillation and sublimation.

Hoping to reduce the limit of error to a still greater degree, we * were led to devise a volumetric method of testing the atomic weight of antimony, which, while it had all the advantages of the gravimetric method previously employed, is free from its sources of error. The method has also this great advantage, that it brings the question of the atomic weight of antimony down to a definite issue.

If the atomic weight of antimony were 122.00, it would require 1.7900 grammes of pure silver to precipitate the bromine from a solution of 2.0000 grammes of antimony bromide, while if the atomic weight of antimony were 120.00, it would require 1.8000 grammes of

* Since publishing our "preliminary notice," our attention has been called to the fact that a similar process was used by Professor J. W. Mallet of the University of Virginia in his investigation of the atomic weight of lithium, as it has since been used by him in his admirable work on the atomic weight of aluminum.

silver. Now it is easy to estimate volumetrically $\frac{1}{100}$ of this difference with certainty. We therefore prepared with great care a button of *pure** metallic silver, which we annealed, and rolled out to a thin ribbon. We then weighed out from two to four grammes of bromide of antimony, prepared by sublimation as described above, and dissolved this salt in an aqueous solution of tartaric acid, which we then transferred to a litre flask, and diluted to about 500 cubic centimetres. We next very accurately weighed out a quantity of silver slightly less than that which calculation showed was required for complete precipitation. This silver was dissolved in nitric acid, and the solution having been evaporated to dryness over a water bath, the silver salt was washed into the flask containing the bromide of antimony. As soon as the supernatant liquid had cleared, the small additional amount of a normal silver solution required to produce complete precipitation was run in from a burette, and measured with the usual precautions. We used no extraneous indicator, because it was important not to introduce any possibly new disturbing element into the experiment, and in the titration of bromine with silver, the normal and familiar phenomena, which mark the close of the process, furnish a very sharp indication. The details of one of the determinations were as follows:—

The weight of the bromide of antimony used amounted to 2.5032 grammes. To precipitate the bromine from the solution of this material, 2.2404 grammes of silver would be required if $\text{Sb} = 122.00$, and 2.2529

* A quantity of silver which had been reduced from chloride and bromide of silver, obtained as a product of previous analytical processes, was dissolved in nitric acid, and precipitated as chloride by hydrochloric acid. The precipitate was first boiled in aqua regia, and then thoroughly washed, after which the chloride was reduced by boiling with caustic soda and inverted sugar, and the precipitate, again washed, having been transferred to a porcelain crucible and dried, was heated to a low red heat in a muffle until the grains were sintered together. The sintered mass was melted on a block of prepared coke before a gas blow-pipe, and while cooling was covered with a reducing flame in order to prevent the occlusion of oxygen gas. The metallic button was next rolled out into a ribbon between steel rollers; and, after the ribbon had been annealed in a muffle, the surface was etched with dilute nitric acid, and afterwards scoured with sand. The metal thus prepared was preserved under distilled water. The oxygen occluded by the metal thus prepared must have been, if any, exceedingly small in amount; but, even allowing the average quantity found by Dumas in metal which had been melted in the air under ordinary circumstances, we calculated that this amount would only affect the third decimal place in the atomic weight of antimony; and it seemed therefore unnecessary to take so inappreciable an effect into consideration. Moreover, the great purity of our material was subsequently made evident.

if $\text{Sb} = 120.00$. We weighed out, with as much accuracy as if we were adjusting a weight, the smaller of these two quantities of metallic silver, and after dissolving the pure metal in pure nitric acid, evaporating the solution to dryness, and redissolving in water, we gradually added the whole of this silver solution to the litre flask containing the solution of bromide of antimony, in the manner described above. It was then found that $12\frac{4}{10}$ cubic centimetres of a standard silver solution (one gramme of silver to the litre) were required to complete the precipitation. It will be seen that the weights of the bromide of antimony and silver used could be thus determined with the most absolute precision, and we have the greatest confidence in these values to the $\frac{1}{10}$ of a milligramme. Moreover, it will be noticed that the volumetric method is only used to estimate the difference in the atomic weight which has been in question, and that, if the method were only accurate to the $\frac{1}{10}$ of the quantity to be measured, it would give us the value of the atomic weight within $\frac{2}{10}$ of a unit, while if, as we had reason to believe, the process was accurate within one per cent, it would fix the atomic weight within $\frac{2}{100}$ of a unit.

By the method just described, the following results were obtained. The letters *a* and *b* indicate different preparations:—

	Wt. of SbBr_3 taken.	Total Wt. of Ag used.	Per cent of Br $\text{Ag} = 108 \text{ Br} = 80$.	Corresponding value of Sb.
<i>a</i> 1.	2.5032	2.2528	66.6643	120.01
<i>a</i> 2.	2.0567	1.8509	66.6620	120.02
<i>a</i> 3.	2.6512	2.3860	66.6644	120.01
<i>b</i> 4.	3.3053	2.9749	66.6696	119.98
<i>b</i> 5.	2.7495	2.4745	66.6653	120.01
Mean value,			<u>66.6651</u>	<u>120.01</u>
Theory Sb. 120 requires			66.6666	
" Sb. 122 "			66.2983	

The extreme variation from the mean in these determinations is less than one ten-thousandth of the quantity directly estimated, and corresponds to less than two ten-thousandths of the total value in the atomic weight of antimony. We have thus reached the extreme limit of accuracy with determinations on this scale. By using very much larger amounts of material, it is possible that we might still further diminish the limits of experimental error; but when we consider the further causes of error incident to handling so large an amount of

material, it seems doubtful whether any advantage would really be gained. At all events such determinations would require an expenditure of labor and skill which is not demanded in the present condition of chemistry.

While making the first three volumetric determinations, it became obvious that the mode of experimenting was highly favorable to the accurate estimation of the amount of bromide of silver formed; and, were we to repeat this investigation, we should adopt the same mode of precipitating bromine in all cases. The rotatory motion given to the liquid mass in the stoppered flask in order to hasten the "clearing up," after each fresh addition of the silver solution, tends very greatly to granulate and thoroughly wash the precipitate. In the last two determinations, therefore, we collected and weighed the bromide of silver formed, and this weight gave us a most important control over the whole work. In the previous work we assume that the ratio of $\text{Ag} : \text{Br} = 108 : 80$, and find that on this assumption $\text{Br} : \text{Sb} = 80 : 120$. But if we both determine the amount of silver required to precipitate a given weight of antimonious bromide, and also at the same time the weight of argentic bromide formed, it is obvious that we fix at once the ratio of three atomic weights ($\text{Ag} : \text{Br} : \text{Sb}$) independently of any assumption whatsoever. This, so far as we know, is a new feature in investigations of this kind, and evidently vastly diminishes the possibilities of error, and enhances the value of the result. We give in full the two determinations which were made in this way:—

No. 1.

Weight of tube and SbBr_3	22.2225	grammes.
“ after transfer to flask	18.9172	“
“ of SbBr_3 taken	3.3053	“
“ of silver taken	2.9749	“
Weight of crucible and filter	44.3729	“
“ “ “ with AgBr dried at 150°	49.5512	“
“ “ “ after again heating	49.5512	“
“ “ AgBr dried at 150°	5.1783	“
Weight of crucible and AgBr after removing } small filter with adhering particles . . . }	49.5008	“
Weight after heating AgBr . to incipient fusion	49.5007	“
Reduced weight of AgBr	5.1782	“
Per cent of bromine	66.665	“
Atomic weight of antimony	120.01	“

No. 2.

Weight of tube and SbBr_3	32.4979	grammes.
“ after transfer to flask	<u>29.7484</u>	“
“ of SbBr_3 taken	<u>2.7495</u>	“
“ of silver taken	<u>2.4745</u>	“
“ of crucible and filter	<u>44.3732</u>	“
“ “ “ with AgBr dried at 150°	<u>48.6810</u>	“
“ “ “ after again heating	<u>48.6810</u>	“
“ “ AgBr dried at 150°	<u>4.3078</u>	“
Weight of crucible and AgBr after removing	} 48.5524		“
small filter with adhering particles			
Weight after heating AgBr to incipient fusion		<u>48.5522</u>	“
Reduced weight of AgBr	<u>4.3076</u>	“
Per cent of bromine	66.667	“
Atomic weight of antimony	120.00	“

Bringing now these results together, we have two additional gravimetric determinations of the atomic weight of antimony.

Weight of SbBr_3 taken.	Weight of AgBr determined.	Per cent of Bromine $\text{Ag} = 108 \text{ Br} = 80.$	Corresponding value of Sb .
<i>b</i> 6. 3.3053	5.1782	66.665	120.01
<i>b</i> 7. 2.7495	4.3076	66.667	120.00
Mean value,		<u>66.666</u>	<u>120.00</u>

It is now obvious that these gravimetric determinations, taken in connection with the corresponding volumetric results, give us the most conclusive evidence of the purity, both of the metallic silver used, and also of the bromine in the bromide of antimony, which is the basis of this atomic weight investigation. By comparing *b* 6 and *b* 7 with *b* 4 and *b* 5 respectively, we obtain the following data:—

1. 2.9749 grammes of silver gave 5.1782 grammes bromide of silver.
2. 2.4745 “ “ “ 4.3076 “ “ “

Hence it follows that, as shown by these experiments, the proportions of the silver to the bromine were respectively:—

1.	108.00	silver to	79.99	bromine.
2.	<u>108.00</u>	“ “	<u>80.01</u>	“
Mean value	108.00	“ “	80.00	“

This is the ratio of the atomic weight of silver to that of bromine, and corresponds to the second decimal place with the determinations of Stas as well as with those of Dumas.

We have now furnished as evidence of the atomic weight of antimony, —

1. The mean of fifteen analyses of bromide of antimony purified by crystallization from sulphide of carbon, with an extreme variation between 119.4 and 120.4 for all the fifteen analyses.

2. The mean of five analyses of bromide of antimony purified by distillation and sublimation, with an extreme variation between 119.90 and 120.08.

3. The mean of five volumetric analyses of bromide of antimony, also purified by distillation and sublimation, with an extreme variation between 119.98 and 120.02.

4. Two gravimetric determinations of the bromine in two of the portions of bromide of antimony used in the volumetric analyses, but still essentially distinct determinations, which gave almost identical results.

Bringing these several means together as of equal value, we have :—

	Percent of Br.	Value of Sb.
1. Mean of fifteen determinations	66.666	120.00
2. “ five “	66.668	119.99
3. “ five “	66.665	120.01
4. “ two “	<u>66.666</u>	<u>120.00</u>
Final mean value,	66.666 +	120.00

Furthermore, we have shown by the last two determinations, that the ratio of the atomic weight of the silver to that of the bromine, used in our experiments, was 108.00 to 80.00, and hence that the ratio of the atomic weights of bromine silver and antimony must be

$$\text{Ag} : \text{Br} : \text{Sb} = 108.00 : 80.00 : 120.00,$$

with a probable error not exceeding 0.01 in any case. Of course our experiments only serve to fix the ratio between these three quantities, and any considerations which may lead chemists to change the value of one of the quantities must affect the other two in the same proportion. If with Stas we take $\text{Ag} = 107.66$, then $\text{Br} = 79.75$, and $\text{Sb} = 119.63$; and in this connection the fact should be recalled that the ratio of Ag to Br, according to Stas, is essentially identical with that given above, and the same as that found both by Dumas and by Ma-

rignac. Of all the ratios between the atomic weights, it is the one in regard to which there is the greatest certainty; and it is with this very well established relation that we have connected the atomic weight of antimony.

Entirely in harmony with the above results are our experiments on the synthesis of sulphide of antimony, in which we found as a mean of thirteen experiments $Sb = 119.94$ when $S = 32$; and the same is equally true of our analyses of iodide of antimony, which gave as a mean of seven determinations $Sb = 119.98$ when $I = 127.00$. But although these results formed important stages in our investigation, they now add but little to the evidence of the far more accordant results since obtained. When compared with these later results they show, however, to what a great extent error may be eliminated by the repetitions of an imperfect process.

Lastly the anomaly which the analysis of antimonious chloride first presented has been explained by finding, first, that the material employed contained a constant amount of oxichloride; and, secondly, that the water used in washing the precipitate exerted a definite solvent action on the chloride of silver estimated.

Having thus solved the problem we undertook as far as is at present practicable, we must now take leave of the subject, regretting only that our investigation should have been the occasion of any controversy. In addition to the recognition we made in our previous paper, we would here express our obligations to Mr. G. De N. Hough and Mr. G. M. Hyams, who have greatly aided us in the experimental work during the latter part of this investigation.

V.—THE BOILING POINT OF IODIDE OF ANTIMONY, AND A NEW FORM OF AIR THERMOMETER.

In continuation of our investigations on the Haloid Compounds of Antimony, the boiling point of antimonious iodide has been determined by Mr. W. Z. Bennett, at the time a student in this laboratory. The observations were made with Regnault's air thermometer, but it was found possible to simplify very greatly the details of the process without seriously impairing the accuracy of the result. For temperatures above the range of a mercury thermometer's measurements, accurate to one degree centigrade, are all that the uncertain conditions of most problems permit, and all, therefore, that the circumstances demand. As used by Regnault, the air thermometer is capable of measuring such temperatures accurately to the one tenth of a degree,

and by multiplying observations possibly to the one hundredth of a degree. In his admirable investigation of the boiling point of sulphur at different temperatures, the observations of temperature are undoubtedly accurate to this extent; but Regnault's own discussion of these observations plainly indicates that there must have been unknown or accidental causes influencing his experiments, which render the results uncertain to at least one degree; and the boiling point of sulphur is still in doubt to this extent. It should be added, however that there are only a very few boiling points which are known more accurately; for, even when within the range of a mercury thermometer, an observation of a boiling point, to be accurate to a tenth of a centigrade degree, requires an attention to circumstances which is seldom bestowed on such observations.

The glass thermometer-bulb used in our experiments is represented in the accompanying figure (Fig. 1) of one half the actual size in its linear dimensions. The longer stem was made of thermometer tube, and a shorter stem was added to the opposite end of the bulb in order to facilitate the cleaning, drying, filling, or emptying of the interior, all of which was easily accomplished by the aid of a Bunsen pump. The shorter stem was of course sealed after the bulb had been dried and made ready for use, and before it was immersed in the medium whose temperature was to be measured. After an equilibrium had been established at this unknown temperature, T'° , the protruding end of the longer stem was sealed, and at the same time the height of the barometer, H , was noted. The bulb was then taken to a room of uniform temperature provided in the laboratory for gas analysis, and, after being mounted on a convenient support, the end of the stem was broken off under mercury, and the apparatus left to itself for a time to secure a perfect equilibrium of temperature. This temperature, T° , was then observed, by means of a standard thermometer



FIG. 1.

hanging near the bulb; also the height, h , to which the mercury had risen in the bulb, was measured by a cathetometer; and in addition the height, H' , of a barometer (hanging in the same room) was noted. Closing now the open stem with the finger, the bulb was quickly inverted and the containing mercury drawn out into a tarred vessel and weighed (nipping off the extreme end of the shorter stem for the purpose). This gave the weight, w . Lastly, the bulb and stem having

been completely filled with mercury by suction, the weight W , corresponding to their total capacity was obtained in a similar way. The required temperature could now be calculated by means of the well-known law of Charles : —

$$T^{\circ'} + 273^{\circ}.2 = (T^{\circ} + 273^{\circ}.2) \frac{W}{W-w} \cdot \frac{H}{H-h} [1 + (T^{\circ} - T^{\circ'}) k]$$

It will be noted that as the mercury columns, including the heights of the barometer, were all measured at the same constant temperature ; and, as we are dealing with relative values only, no reductions are necessary. Moreover, an error of one tenth of a millimetre in the value of $\frac{H}{H-h}$ would make, in determining the boiling point of sulphur (448°), a difference of only one eighth of a degree, so that measurements of these heights are sufficiently close, if accurate, to one half a millimetre, and might even be made with a common rule. The most uncertain element in the formula is the expansion of glass ; but if the bulbs are made of flint glass (lead glass) tubing, such as is used in this neighborhood for ornamental ware, the mean coefficient of expansion will vary very little from 0.000025, if the temperature does not exceed that at which the glass begins to soften. The rate of expansion of flint glass is not only less than that of crown, but it is also more constant, and increases very slowly with the temperature. Flint glass is therefore better adapted for the use we are describing. The expansion of the glass used in our experiments was carefully determined, and found to have the value given above, within two or three tenths of a unit in the last place. A difference of one unit in this place would make a difference of one third of a degree in the boiling point of sulphur.

In order to test the accuracy of this method, Mr. Bennett made four determinations of the boiling point of sulphur under different barometric conditions, which in the following table are compared with the results of Regnault, reduced to the corresponding pressures : —

Barometer. Height at 0°.	Boiling Point of Sulphur.		
	Bennett.	Regnault.	Diff.
758.8	447.4	447.3	+ 0.1
763.9	448.2	447.7	+ 0.5
769.6	448.2	448.1	+ 0.1
776.7	448.2	448.7	— 0.5

Regnault made eight observations on the maximum tension of sulphur vapor at temperatures varying from $387^{\circ}.64$ to $554^{\circ}.03$, and from a discussion of these deduced the constants of an exponential formula, by which he calculated a table of maximum tensions for every ten degrees between the extreme limits, and also plotted a corresponding curve. It so happens, however, that the only two observations within the range of ordinary atmospheric pressure fall outside, and on the same side, of this assumed curve. These observations are the ones usually taken as indicating the boiling point of sulphur; and Victor Meyer, in one of his methods of determining the density of the vapors of substances which have a high boiling point, assumes a value for the boiling point of sulphur (at the mean atmospheric pressure at Zurich), which he obtains by simple interpolation from the two observations just referred to.* In like manner we have calculated the above values corresponding to the pressures at which Mr. Bennett's results were obtained on the basis of the same two observations; but, instead of simply interpolating by the first differences, we have assumed that the variation between the two observed values would follow the law indicated by the general curve, which Regnault gives as the best expression for all his observations. But according as we take the two observations, or the whole, we obtain values for the boiling point of sulphur differing by more than a degree; and hence, as we have already said, there is still an uncertainty in regard to the boiling point to this extent. As is evident, Mr. Bennett's observations confirm very closely the interpretation of Regnault's results, adopted by both Victor Meyer and by ourselves.

After the accuracy of our method had been thus placed beyond doubt within the limits required, Mr. Bennett made three determinations of the boiling point of antimonious iodide, with the following results:—

Barometer.	Height at 0° .	Boiling Point of Sb T_3 .
	758.1 millimetres.	$400^{\circ}.4$
	758.4 “	$400^{\circ}.9$
	759.3 “	$400^{\circ}.9$

Probably only a small part of the difference between these observations depends on the variations of pressure. We only regard the method as accurate to whole degrees, and 401° is evidently the boiling

* Fresenius's Zeitschrift, xvi. 482.

point of antimonious iodide at the normal pressure of the air within half a degree on either side.

The method we have here described we can most confidently recommend as a most efficient and accurate means of determining high temperatures in chemical laboratories. It requires no expensive apparatus, and no more delicate manipulation than most processes of gas analysis. Indeed, this method is most readily associated with Bunsen's methods of gas analysis; and, in a laboratory provided with a room fitted for that work, the observation of temperature we have described can be made in a very short time.

In connection with these experiments, we were led to devise a very simple and inexpensive form of differential air thermometer, that can be used almost as readily as a mercury thermometer, and which will measure either high or low temperatures with all the accuracy that is usually required. The instrument is represented by Fig. 2 of one half its linear dimensions. The long stem is made of "barometer tubing," a little over a millimetre in diameter, and by careful calibration is arbitrarily divided into parts of equal capacity, making, we will say, two hundred divisions on the length of the stem. While the instrument is still open at both ends it is easy to determine, first, the weight of mercury which fills the bulb up to the first division of the stem; and secondly, the weight of a column of mercury covering an observed number of divisions of the stem. These constants being known, and the interior of the instrument having been most carefully dried, for which the two openings offer great facilities, a short column of very pure mercury is introduced, and brought into the position represented in the figure. The two ends are now hermetically closed with a blow-pipe, and the instrument is made. It can be used either in a vertical or horizontal position, although the zero point of the scale is slightly different in the two cases, owing to the weight of the short mercury column. Of course this column remains immovable so long as the temperature of the two ends remains the same; but when the bulb is heated, the column, which we will call the index, moves up the stem, which becomes a closed monometer. If the instrument is to be used for measuring low temperatures, the index should be placed about one third way up

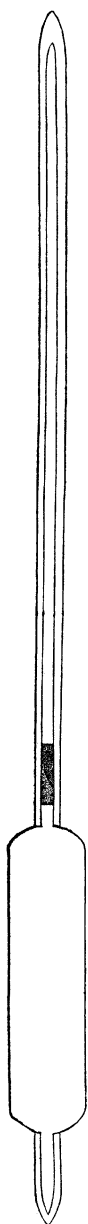


FIG. 2.

the stem before closing the open ends. The theory of the instrument is the same in either case, but in our description we will assume that the index has been set for measuring high temperatures, as shown in our figure.

As the instrument is a differential thermometer, its accuracy depends on keeping the stem at a *constant* and *known* temperature; and from this constant temperature the observed temperatures are deduced. When the thermometer is held in a horizontal position, and the stem can be protected from the neighboring sources of heat, it is sufficient to place a standard mercury thermometer at the side of the stem; but it is always better, and generally necessary, when the stem is in a vertical position over the source of heat, to surround the stem with a jacket, through which circulates a stream of water of known temperature. This temperature we will call the temperature of reference, and represent by T° . In order now to determine the value in centigrade degrees of the division of the instrument, we place it in the position in which we propose to use it; and when the two ends are at the same temperature, we observe the position of the two ends of the index on the graduate scale. We can now easily find from the weights obtained before closing the instrument, first the weight of mercury which would fill the bulb and stem up to the index, which we call W ; and, secondly, the small weight of mercury which would fill one division of the stem which we will call w . We have also, by observation, the number of division on the stem above the index. This number, which we count from the closed end of the stem, we will represent by N .

Assume now that the bulb and stem up to the index is immersed in a medium which has the temperature, T' . The index moves, and in its new position let N' represent the number of division on the stem above the index. We can now easily deduce the following values:—

$\frac{N}{N'}$ = the ratio of the tension of the confined air at T'° and T° .

$N - N'$ = the number of division through which the index moved.

$\frac{W + (N - N') w}{W}$ = the ratio of the volumes of the air in the bulb at T° and T'° , independent of the expansion of the glass.

$\frac{W + (N - N') w}{W} (1 + [T - T'] k) =$ same ratio, allowing for expansion of glass.

Then, as we can easily deduce from the laws of Mariotte and Charles:—

$$T''^{\circ} + 273 = \frac{N}{N'} (T^{\circ} + 273) \frac{W + (N - N') w}{W} (1 + [T^{\circ} - T''^{\circ}] k)$$

With this formula, it is now easy to compute the values for each division of our arbitrary scale. We cannot, however, depend absolutely on the result, as there are several causes which will differ with each instrument, and of which we can take no account. It is therefore best to observe, with the instrument, two or three well-established boiling points, which will give us fixed points by which we can correct the table, and we shall then have an instrument whose precision is fully equal to that of a mercury thermometer.

It is, of course, very desirable that the temperature of reference T° should be always the same and as invariable as possible. This is best accomplished, as above suggested, by maintaining a circulation of water through a glass jacket surrounding the stem of the instrument and enclosing also a small mercury thermometer, which is best tied to the stem. By selecting the temperature of reference a little higher than the highest temperature of the water supplied by the laboratory hydrants, it is easy to maintain the required temperature within a degree by regulating the flow. The instrument may then be adjusted to the tubulature of a retort and used in fractional distillations.

VI. REVISION OF THE ATOMIC WEIGHT OF CADMIUM.

By OLIVER W. HUNTINGTON, *of the Senior Class.*

THE method adopted by Professor Cooke for verifying the value of the atomic weight of antimony, described in this volume (page 16), proved to be so definite and conclusive, that it seemed desirable to apply it in all other cases to which it was suited, in order not only to verify the received values of the atomic weights, but also to test more fully the hypothesis of Prout, an hypothesis to which recent investigation and speculations have given renewed interest.*

The method of Professor Cooke is applicable to all those elements of which a pure, stable, well-defined, and soluble bromide can be pre-

* See Revision of the Atomic Weight of Aluminum, by J. W. Mallet, *Philosophical Transactions*, part iii. 1880: also various papers by J. Norman Lockyer on the disassociation of the chemical elements in "Nature" and in the *Proceedings of Royal Society*; also Cooke's *Chemical Philosophy*, revised edition, page 272.

pared. It consists in determining in one series of analyses the bromine of the compound as bromide of silver by the usual gravimetric method with the precautions already described (page 19); and in another series of experiments, or in the same analyses, when practicable, determining the amount of silver required to precipitate the bromine. We thus obtain not only the relation of the atomic weight sought both to that of bromine and to that of silver; but also the relation between the atomic weight of bromine and that of silver; and since all experimenters agree on this last ratio to within one ten-thousandth of its value it is evident that the comparison of the two series of results gives a sharp control of the accuracy of the work.

Professor Cooke assigned to me the atomic weight of cadmium as my portion of the work he had planned on the revision of the atomic weights, and this investigation was made with his aid and under his immediate direction. Bromide of cadmium fulfils all the conditions which the new method requires; and, since the accepted value of the atomic weight of cadmium is a whole number, it seemed probable that a revision of this value by a more exact process would bring additional evidence in support of the hypothesis of Prout.

Having found that bromide of cadmium could not readily be purified by repeated crystallizations on account of its very great solubility in water, we sought to obtain a pure compound by preparing pure carbonate of cadmium on the one hand and pure hydrobromic acid on the other.

To prepare pure carbonate of cadmium the commercial metal was first dissolved in pure hydrochloric acid. From this solution, still strongly acid, sulphide of cadmium was precipitated by sulphide of hydrogen, and the precipitate thoroughly washed with hot distilled water. The sulphide having been redissolved in hydrochloric acid, and the resulting sulphide of hydrogen expelled by boiling, the cadmium was next precipitated as carbonate by carbonate of ammonia, and the precipitate digested with a large excess of this reagent. The white carbonate thus obtained was thoroughly washed and redissolved in hydrochloric acid; and the same series of precipitations repeated. Lastly, in order to remove any possible trace of adhering chloride, the carbonate of cadmium which had thus been twice precipitated by carbonate of ammonia, and twice digested with a large excess of this reagent, was dissolved in pure hydrobromic acid, and a third time precipitated and digested with pure carbonate of ammonia.

The hydrobromic acid used in this investigation was made by the process described by Dr. Edward R. Squibb, of Brooklyn, in the

Transactions of the Medical Society of the State of New York.* In order to purify the acid, it was repeatedly redistilled with a small amount of a concentrated solution of bromide of potassium, rejecting each time the distillate until the boiling point rose to 128° ; when, as is well known, an acid containing about 47 per cent of HBr distills unchanged. The acid thus obtained was as colorless as water.

Meanwhile, in order to test the purity of the hydrobromic acid and also as a basis for the rest of our investigation, we prepared a quantity of pure silver by the method already fully described in a previous part of this volume (page 17); and with the pure silver thus prepared the following two sets of determinations were made.

For the first set, weighed amounts of silver were dissolved in very carefully purified nitric acid, using only a very slight excess of this solvent in any case. We prepared for the purpose a dilute acid by mixing one part of acid, having Sp. Gr. 1.355, with four parts of water and of this weak acid 5.3 c. m.^3 were required for each gramme of silver. We were thus able to estimate the amount necessary for each analysis, and we used generally one half a cubic centimetre in excess.

The silver having been perfectly dissolved, and the solution diluted with water to from two hundred to five hundred cubic centimetres, according to the amount of silver used, we gradually and cautiously precipitated bromide of silver by adding pure hydrobromic acid, prepared as just described, but greatly diluted until the acid was very slightly in excess. For the method of washing and collecting this

* "The formula and process for making an acid of this strength are as follows:—

Take of Potassium Bromide	Six parts.
Sulphuric Acid, Sp. Gr. at $15^{\circ}.6 \text{ C.}$ }	. . . Seven parts.
1.838, at 25° C. 1.828	
Water	Nine parts.

"Add to the sulphuric acid one part of the water and cool the mixture. Then dissolve the potassium bromide in six parts of the water by means of heat, supplying the loss of water by evaporation during the heating. Pour the diluted sulphuric acid slowly into the hot solution with constant stirring, and set the mixture aside for twenty-four hours, that the sulphate of potassium may crystallize. Pour off the liquid into a retort, break up the crystalline mass, transfer it to a funnel, and, having drained the crystals, drop slowly upon them two parts of the water so as to displace and wash out the acid liquid. Add the liquid, thus drained off and washed out, to that in the retort, and distil the whole nearly to dryness, or until nothing further distills off by moderate heating. The distillate will weigh about ten parts and should contain about thirty-seven per cent of hydrobromic acid."

precipitate, we may refer to Vol. XII. page 124, of these Proceedings. The results were as follows:—

	Weight of Silver.	Weight of Bromide of Silver.	Per Cent of Silver.
1.	1.4852 grammes.	2.5855 grammes.	57.444
2.	1.4080 “	2.4510 “	57.446
3.	1.4449 “	2.5150 “	57.451
	Mean Value		<u>57.447</u>

For the second set of experiments bromide of silver precipitated, washed, and dried as described (*loc. cit.*), was melted in a platinum crucible, and then reduced by a voltaic battery under dilute sulphuric acid. This process was devised and perfected by Mr. L. P. Kinnicutt, Assistant in this Laboratory, who had the great kindness to conduct the reduction in the following determinations.

	Weight of Bromide of Silver.	Weight of Silver.	Per Cent of Silver.
1.	4.1450 grammes.	2.3817 grammes.	57.444
2.	1.8172 “	1.0437 “	57.434
3.	4.9601 “	2.8497 “	57.449
	Mean Value		<u>57.442</u>

These results show conclusively the great accuracy of Mr. Kinnicutt's process, which he will describe in detail in another place. The mean of the two sets of results gives for the per cent of silver 57.445, the theoretical per cent ($\text{Ag} = 108$ and $\text{Br} = 80$) being 57.446. If we throw out No. 2 of second series, which is obviously less trustworthy than the other two determinations of the same series, on account of the comparatively small amount of material used, the mean of the remaining five determinations corresponds absolutely to theory, and the total result, therefore, leaves no doubt whatever as to the absolute purity of the materials employed.

Bromide of cadmium was now prepared by dissolving pure carbonate of cadmium in pure hydrobromic acid, and subliming the product previously dried at 200° in a current of pure and perfectly dry carbonic dioxide gas. The carbonic dioxide was prepared by mixing bicarbonate of soda and sulphuric acid with a large volume of water in a strong generator, and drawing off the gas under pressure through appropriate washers and driers; and the apparatus used for subliming the bromide of cadmium was similar to that described in these Proceed-

ings, Vol. XIII. page 57, using however a porcelain tube heated by a gas furnace in place of a tube of glass. The bromide of cadmium when thus sublimed crystallizes in pearly scales around the open mouth of the tube.

Prepared as we have described, anhydrous bromide of cadmium is a splendid preparation. The precise form of the highly lustrous crystals could not be distinguished, but the scales are tabular crystals having a single optical axis normal to the extended face of the scales and having a high negative double refracting power. Although so soluble, the crystals are not sensibly hygroscopic, and can be weighed on an open watch-glass without the slightest variation of weight during the process. They dissolve at once in water without leaving a trace of residue.

The following determinations were all made with the material we have described, and since only a few grammes could be sublimed at a time, the separate analyses were made with the products of nearly as many sublimations. Some of the material was sublimed twice, and the constancy of the composition under these circumstances is the best proof possible of the definiteness of the compound. The results of the analyses may be classed under two heads.

In one series of determinations, the bromide of antimony, whose weight had been accurately determined, having been dissolved in pure water in a stoppered flask, a little less than the calculated amount of silver required to precipitate the bromide was carefully weighed out and dissolved in a measured amount of weak nitric acid allowing as before described a slight excess. This solution properly diluted was then gradually added to the solution of bromide of cadmium under constant agitation in order to avoid the aggregation of the bromide of silver in lumps. The agitation was frequently renewed until the precipitate settled, and then a standard solution of silver (one gramme to the litre) was cautiously added until the precipitation was complete, and the last drops did not produce the faintest opalescence after standing. The precipitate was now washed by decantation five times successively, using each time a volume of cold distilled water equal to the volume of the original solution, and pouring off the water into a porcelain crucible, from which it was drawn by the reverse filter. Finally, the precipitate was washed into the crucible, and after drying at from 120° to 130° weighed with the small filter.

In a second series, the determinations were conducted in the same way as in the first, excepting that the chief attention was directed to determining the exact point of complete precipitation. In several cases, indicated by an asterisk, both the amount of silver required, and

the amount of argentic bromide formed were determined in the same experiment; but this was not always practicable.

FIRST SERIES.

	Weight of Bromide of Cadmium.	Weight of Bromide of Silver found.	Value of Cd when Ag = 108 and Br = 80
1.	1.5592 grammes.	2.1529 grammes.	112.32
2.*	3.7456 “	5.1724 “	112.28
3.	2.4267 “	3.3511 “	112.28
4.*	3.6645 “	5.0590 “	112.36
5.*	3.7679 “	5.2016 “	112.36
6.	2.7938 “	3.8583 “	112.27
7.*	1.9225 “	2.6552 “	112.26
8.	3.4473 “	4.7593 “	112.34
Mean Value			<u>112.31</u>

SECOND SERIES.

	Weight of Bromide of Cadmium.	Weight of Silver required.	Value of Cd when Ag = 108 and Br = 80
1.*	3.7456 grammes.	2.9715 grammes.	112.27
2.	5.0270 “	3.9874 “	112.30
3.*	3.6645 “	2.9073 “	112.26
4.*	3.7679 “	2.9888 “	112.30
5.*	1.9225 “	1.5248 “	112.33
6.	2.9101 “	2.3079 “	112.35
7.	3.6510 “	2.8951 “	112.39
8.	3.9782 “	3.1551 “	112.35
Mean Value			<u>112.32</u>

As can easily be calculated according to the mean of the first series of determinations, 1.0000 gramme of bromide of cadmium gives 1.3808 grammes of argentic bromide, and according to the mean of the second series 1.0000 gramme of bromide of cadmium requires for complete precipitation 0.7932 gramme of silver. Hence, as a mean of these experiments, 0.7932 gramme of silver yields 1.3808 grammes of argentic bromide and therefore corresponds to 0.5876 gramme of bromine. Moreover, since

$$0.7932 : 0.5876 = 108.000 : 80.006,$$

it follows with a very high degree of probability that

$$\text{Ag} : \text{Br} : \text{Cd} = 108.00 : 80.00 : 112.31,$$

within one ten-thousandth of the value of either quantity. It must of course be regarded as absolutely proved that, in the material analyzed, the proportion of bromine to the remainder of the mass, assumed to be pure cadmium, is as 2×80.00 to 112.31, but it is always conceivable that the material used contained some unknown impurity. In the present case, however, such an assumption is highly improbable; first, because such extreme care was taken in the preparation; secondly, because the products of the different sublimations were so constant in composition; and, thirdly, because the presence of any of the metals usually associated with cadmium would tend to lower and not to raise the apparent atomic weight. If any impurity is present, it would seem as if it must be some unknown element, and only on such a bare chance as this can the evidence be invalidated which the results of this investigation furnish against the hypothesis of Prout.